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Solventless Manufacture of Artillery Propellant Using Thermoplastic Elastomer Binder, PP-867

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13. ABSTRACT ***(Maximum 200 Words)***
Multi-base gun propellant for artillery ammunition creates 0.3 lb of solvent emissions per lb of propellant, and at expected production rates of 3 million lb/yr, this represents the largest source of VOC emissions due to gun propellant production. New thermoplastic elastomer (TPE) binders are available which should make it possible to develop and manufacture gun propellants that are producible without solvent emissions. These binders may be useable in a variety of other energetic material applications, including rocket propellants, explosives and pyrotechnics. In addition to solvent reduction or elimination, TPE binders may permit recovery and recycling of propellant ingredients for additional pollution prevention. To date, these TPEs have not been qualified for use in military ordnance systems, largely due to the perceived risk of using novel materials and manufacturing processes.

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Annual Technical Report for FY98

Project title: Solventless manufacture of artillery propellant using thermoplastic elastomer binder, PP-867

Performing organizations:

Lead laboratory: Naval Air Warfare Center Weapons Division, China Lake, CA

Other performing organizations:
Naval Surface Warfare Center Indian Head Division
Army Armament Research, Development and Engineering Center
Stevens Institute of Technology

Project background:

Multi-base gun propellant for artillery ammunition creates 0.3 lb of solvent emissions per lb of propellant, and at expected production rates of 3 million lb/yr, this represents the largest source of VOC emissions due to gun propellant production. New thermoplastic elastomer (TPE) binders are available which should make it possible to develop and manufacture gun propellants that are producible without solvent emissions. These binders may be useable in a variety of other energetic material applications, including rocket propellants, explosives and pyrotechnics. In addition to solvent reduction or elimination, TPE binders may permit recovery and recycling of propellant ingredients for additional pollution prevention. To date, these TPEs have not been qualified for use in military ordnance systems, largely due to the perceived risk of using novel materials and manufacturing processes. A demonstration of the feasibility of using TPEs in a solventless process will lower the perceived risk and accelerate acceptance and use of these promising materials and processes.

Propellant manufacture by continuous, twin screw extrusion has been considered as an alternative to conventional, batch processing (Husband, 1989; Murphy et al, 1991). Important considerations for gun propellant manufacture in twin screw extruders include control of the feed rate of raw materials, proper configuration of the screws, and predictable, stable flow through the extrusion die. Each of these issues will be addressed in this project.

Objective:

The objective is to demonstrate the feasibility of reducing or eliminating the emission of volatile organic compounds (VOCs) and solvents associated with the production of gun propellants by using thermoplastic elastomer (TPE) propellants. New propellant formulations that reduce or eliminate the use of solvents will be developed and evaluated for potential replacement of current propellants that require solvents to manufacture. This project will demonstrate at a pilot plant scale the production of TPE gun propellant by using solventless continuous processing.

Technical approach:

New TPE propellant formulations are being designed to permit solventless processing while simultaneously meeting performance and safety requirements. This requires evaluating the most promising TPEs, determining the proper composition and molecular weight of the TPE, and optimizing the choice and amount of oxidizer in the propellant. A solventless manufacturing process is being developed for this propellant by modifying and adapting existing continuous twin screw extrusion technology. Manufacture of the new

TPE propellant by the solventless process will be demonstrated at a pilot plant scale. The manufacturability, safety, sensitivity and performance properties of the propellant produced will be evaluated in proof of principle tests.

For leveraging cost of testing and evaluation this project is closely coordinated with efforts to develop a propellant charge for the Crusader 155-mm howitzer, as well as with related projects, including the ARDEC 6.2 Technology Base Program, the Green Energetics Affordability Initiative, and other efforts to develop propellants for naval guns and tank guns. Developments are communicated to the user community through briefings, workshops, and professional society presentations and publications. Under leveraged funds, sufficient propellant for approximately fifteen rounds is being manufactured, and these rounds will be fired in a 155-mm gun to evaluate actual propellant performance. These results will guide further improvement of the propellant composition and manufacturing process. Technology developed under this SERDP project will be transferred through briefings and reports to the Crusader Program and through discussions with representatives of the Army ammunition plants and the Army Single Manager for Conventional Ammunition.

In FY98, TPE propellants were more fully characterized for processability, safety, and performance in order to enable the choice of a composition to demonstrate solventless processing in FY99. Characterization included rheological and thermal testing of the molten propellant, as well as studies of burn rate, mechanical properties, sensitivity, and safety properties. A mathematical model of the capillary viscometer at the Naval Surface Warfare Center-Indian Head Division (developed under leveraged funds) is being used to enable better interpretation of data from rheological and processability studies. Use of plasticizer was examined for improving properties at low and high temperatures. To define the solventless manufacturing process, extrusion dies are being designed using computational fluid dynamics models developed in FY97 by the Stevens Institute of Technology. Raw materials handling studies were performed to define feeder requirements and operating conditions.

Project accomplishments:

Progress was made in evaluation of new TPE propellant compositions and studying the feeding behavior of raw ingredients. The Naval Surface Warfare Center-Indian Head Division (NSWC-IHD) evaluated several batches of TPE propellant, including effects of varying placticizer and solids content of Hytrel® based propellants. At the same time, under the Army Armament Research, Development and Engineering Center (ARDEC) Technology Base funding, Thiokol Corp. prepared small batches of BAMO-AMMO propellant with promising properties.

In order to select the composition to be used in the solventless process demonstration and in gun firings, the properties of several TPE propellant compositions using two TPE binders were evaluated. The binders were Hytrel® polyether-polyester block copolymer made by DuPont, and poly(3,3-bisazidomethyl oxetane)-poly(3-azidomethyl-3-methyl oxetane) block copolymer (BAMO-AMMO), made by Thiokol Corp. The Hytrel® TPE has the advantage of lower cost, but is less energetic, which constrains the range of compositions that can supply the required performance while remaining processable without solvent. The results of earlier work on these TPEs are described in Harris, et al. (1996 and 1997). The compositions to be evaluated used the oxidizers RDX and nitroguanidine (NQ). These ingredients were selected on the basis of required energy and burning rate.

This year, work was focused on selecting a suitable composition to use for the planned solventless process demonstration and in gun firings. The Hytrel® compositions evaluated

in FY97 had shown processing advantages of using high-bulk-density nitroguanidine (HBNQ) over conventional NQ, owing to the approximately spherical shape of the HBNQ as opposed to the needle-like conventional NQ. These propellants were characterized further this year. Their compositions are shown in Table 1.

Table 1. Hytrel® TPE propellant compositions
(percentages by weight)

	IH94097F-TPEMA-0661	IH94097F-TPEMA-0662
Hytrel®	12.82	12.82
acetal/formal	10.26	10.26
RDX (5 mμ)	57.69	57.69
HBNQ	19.23	-
NQ	-	19.23

Thermal properties were acceptable, but burn rate measurements performed at ARDEC were inconclusive. NSWC-IHD repeated the burn rate measurements in a closed bomb at ambient temperature at pressures from 8000 to 70,000 psi. The measured burn rates are shown in Table 2, and the plots are given in Figures 1 and 2. Preliminary analysis of burn rate data and qualitative examination of the Hytrel® propellant indicate that mechanical strength of the propellant strands may be insufficient and that the propellant may be breaking up during the burn measurements.

Table 2. Burning rate of Hytrel® TPE propellant compositions

	burning rate coefficient	burning rate exponent
IH94097F-TPEMA-0661	1.567E-4	1.22
IH94097F-TPEMA-0662	1.057E-5	1.04

Based on thermochemical calculations and empirical knowledge of processing characteristics of similar compositions, NSWC prepared two batches of propellant containing Hytrel®, with different amounts of acetal/formal (A/F) plasticizer and oxidizer. A mix was also made substituting triethylene glycol dinitrate (TEGDN) for some of the acetal/formal (A/F) to see if improved properties could be obtained with this different plasticizer. Measurements made at the Naval Air Warfare Center-Weapons Division (NAWC-WD) have shown that TEGDN lowered viscosity and glass transition temperature of Hytrel® more effectively than A/F. The formulations and thermochemical calculations are shown in Table 3. It was found that mixing and extruding these compositions without solvent was difficult. Although with reworking, well-consolidated strands were successfully extruded (without solvent), further work on Hytrel® TPE propellants was clearly needed to develop a suitable composition using Hytrel®. Progress made on BAMO-AMMO propellants to date (discussed below) indicates that adequate properties can be achieved with this TPE, and NSWC-IHD has some experience in processing BAMO-AMMO in the twin-screw extruder, so the choice of BAMO-AMMO as the binder for gun firings and process demonstration was considered lower risk for this project. Therefore, no further formulation and characterization of Hytrel® TPE propellant was pursued. However, the use of Hytrel® for gun propellant binder should not be ruled out, since it may offer a lower cost alternative to BAMO-AMMO.

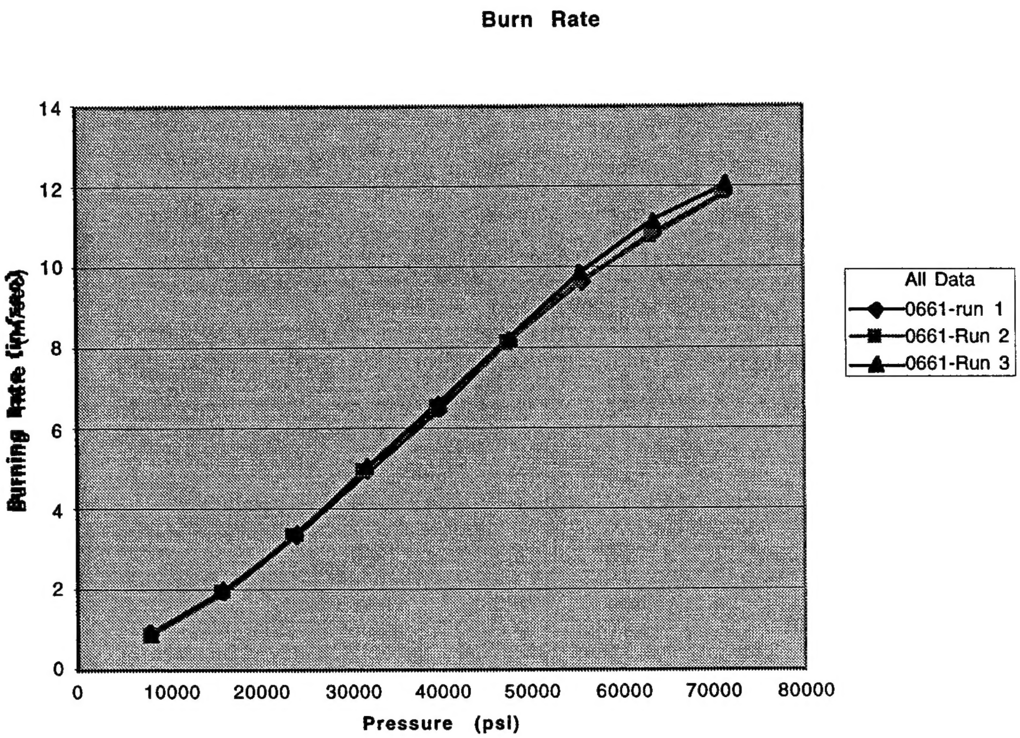

Figure 1. Burn rate of Hytrel® composition IH94097F-TPEMA-0661 listed in Table 1.

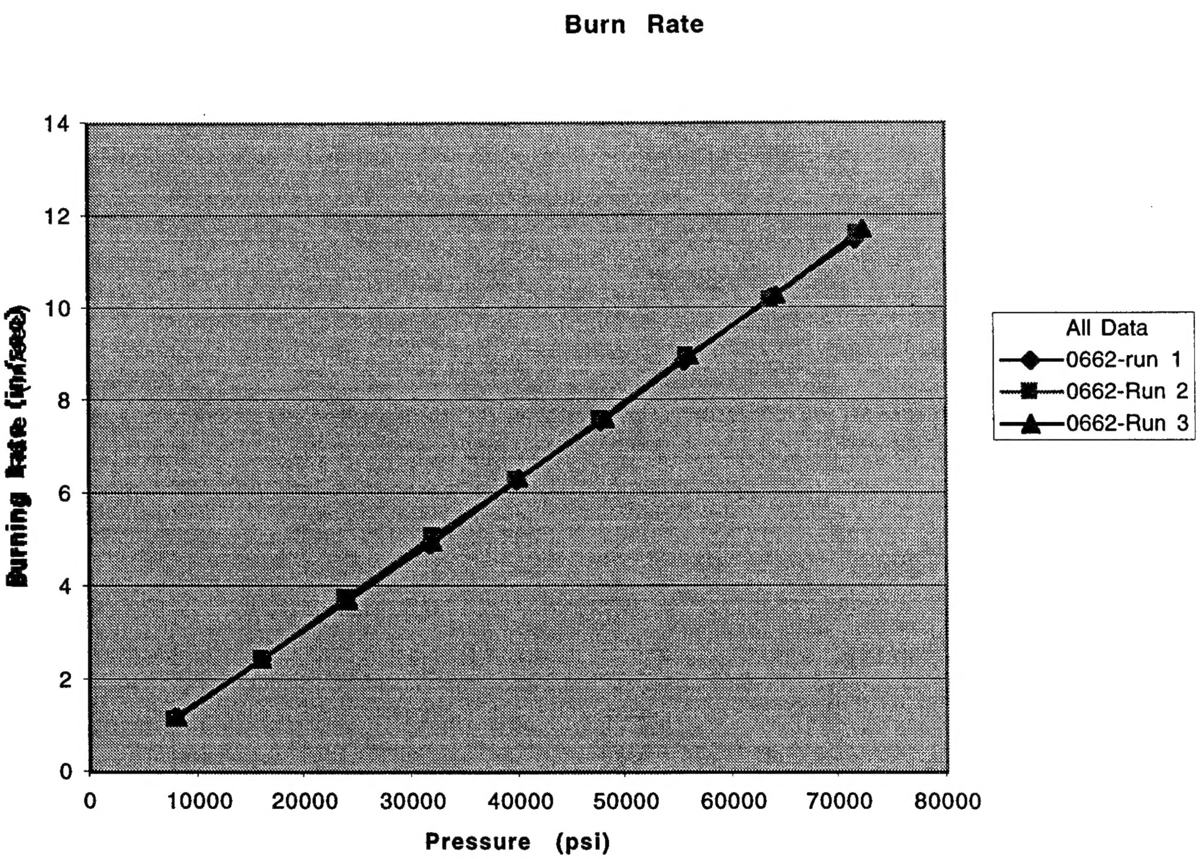

Figure 2. Burn rate of Hytrel® composition IH94097F-TPEMA-0662 listed in Table 1.

Table 3. Alternate Hytrel® TPE propellant compositions and calculated properties

	"Standard" Hytrel Formulation	IH94097M-TPEMA-0000	IH94098C-TPEMA-0028	IH94098C-TPEMA-0029
Density (g/cc)			1.55	1.66
Tv	2523	2510	2648	2785
Isp	1037	1034	1078	1117
g	1.275	1.275	1.272	1.267
CoVol (g/cc)	1.191	1.19	1.181	1.166
MW	20.21	20.18	20.421	20.733
Hytrel	12.82	12.82	12.71	11.39
5 μ RDX	57.69	57.69	64.21	66.92
A/F	10.26	5.13	11.04	9.16
TEGDN		5.13		
NQ/HBNQ	19.23	19.23	12.04	12.53

Under leveraged Army funds, Thiokol Corp. prepared two small batches of BAMO-AMMO propellant, one with conventional NQ and one with HBNQ. Preliminary characterization confirmed the improvements obtainable with HBNQ over conventional NQ. NSWC-IHD also prepared two small (~80g) batches of BAMO-AMMO propellant, with the composition shown in Table 4. Graphite was used in anticipation that in a continuous process, the graphite would be required as a partitioning agent to keep the BAMO-AMMO free-flowing in the feeding equipment. The two batches were of the same composition, but were prepared from different ingredient forms. One was prepared from individual raw ingredients and the other from a propellant containing BAMO-AMMO/RDX and additional raw materials required to match the desired composition. Both batches were processed without solvent. Preliminary safety measurements on these two batches are shown in Table 4. This is the composition to be used in the processing demonstration and gun firings.

Table 4. BAMO-AMMO TPE propellant compositions, one (-0053) made by reformulating existing propellant, and one (-0054) made from raw ingredients, with measured safety properties (compared with pure RDX standard)

	IH94098 - BAT5R-0053	IH94098 - BAT5R-0054	RDX 'A'Standard
65/35 BAMO/AMMO + Graphite	1.07%	19.96%	
5μ RDX	---	59.76%	
BAMO-AMMO/RDX Gun Propellant*	78.95%	---	
HBNQ	19.98%	19.98%	
NOS Impact (mm)	211	220	220
ABL Friction (psig)	420	750	235
ABL ESD (J)	0.165	0.037	0.037

*75.7% 5μ RDX, 23.9% 65/35 BAMO-AMMO, 0.4% Graphite

A larger batch (~8 lb) of BAMO-AMMO propellant was produced using BAMO-AMMO/RDX propellant as a starting material. Flow measurements on this propellant was performed in a capillary viscometer at NSWC-IHD. Data are being reduced at the Stevens Institute of Technology to determine viscosity as a function of shear rate and temperature and wall slip as a function of wall shear stress. These results will be used in extrusion die flow simulations performed by Stevens institute to support extrusion die design.

NSWC completed the planned feeder studies. Hytrel® TPE and HBNQ could be fed continuously using existing equipment at the mass flow rates desired, but NQ could not be accurately fed using existing equipment. While modifications to the feeding equipment may make it possible to accurately feed NQ, such a development effort would be too ambitious for the budget and schedule of this project. A method for continuously feeding BAMO-AMMO TPE was developed by NSWC under a related effort (the Affordability Initiative Green Energetic Materials project). Cryogenic grinding the BAMO-AMMO and coating it with graphite gave a flowable form that was accurately feedable.

Conclusions:

Improved TPE propellant compositions were characterized to support the solventless process development. Propellants containing Hytrel® poly(ether)-poly(ester) TPE were evaluated for processablity and burn rate, and were found to be more difficult to process without solvent than propellants containing BAMO-AMMO. BAMO-AMMO propellants were mixed and extruded without solvent and characterized for processability. It appears that it may be feasible to reformulate TPE propellant from existing propellant by solventless mixing. Raw materials handling studies showed the feasibility of continuously feeding HBNQ, but feeding conventional NQ was found to be more difficult to feed. The propellant composition to be used in the processing demonstratoin and gun firings was chosen and contains BAMO-AMMO, RDX and HBNQ.

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Harris, L. E., T. Manning, K. Klingaman, R. B. Wardle, J. P. Braithewaite, T. Stephens, and S. Prickett, "Thermoplastic Elastomer (TPE) Gun Propellant," Proceedings of the 1997 JANNAF Combustion Subcommittee Meeting, West Palm Beach, FL, Oct 97, CPIA Publication.

Harris, L. E., S. Moy, T. Manning, R. B. Wardle, A. Haaland, J. A. Hartwell, T. Stephens, C. Murphy and S. Prickett, "Thermoplastic Elastomer (TPE) Artillery Propellant," 1996 JANNAF Propulsion Meeting, Albuquerque, NM, 9-12 Dec, CPIA Publication 650.

Husband, D., M., (1989) "Continuous Processing of Composite Solid Propellants," Chemical Engineering Progress, May, pp 55-61.

Murphy, C., S. Brown, C. Oden, R. Muscato, (1991) "LOVA Continuous Processing," Naval Ordnance Station Technical Report, IHTR 1462, 13 May.

Appendix - FY98 Publications and Presentations

Paper (unrefereed):

Harris, L. E., T. Manning, K. Klingaman, R. B. Wardle, J. P. Braithewaite, T. Stephens, and S. Prickett, "Thermoplastic Elastomer (TPE) Gun Propellant," Proceedings of the 1997 JANNAF Combustion Subcommittee Meeting, West Palm Beach, FL, Oct 97, CPIA Publication.

Presentation:

Harris, L. E., T. Manning, K. Klingaman, R. B. Wardle, J. P. Braithewaite, T. Stephens, and S. Prickett, "Thermoplastic Elastomer (TPE) Gun Propellant, presented at The Joint Ordnance Commanders Group Explosives and Propellants Sub-Group Meeting, 7-9 April 1998, Naval Surface Warfare Center, Indian Head, MD.